비수계 전해액을 사용한 리튬이온전지의 안전성 향상을 위한 설계 및 특성평가

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Design and Characterization for Safety Improvement of Li-Ion Batteries Using Nonaqueous Electrolytes

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Korea Electrotechnology Research Institute (KERI)

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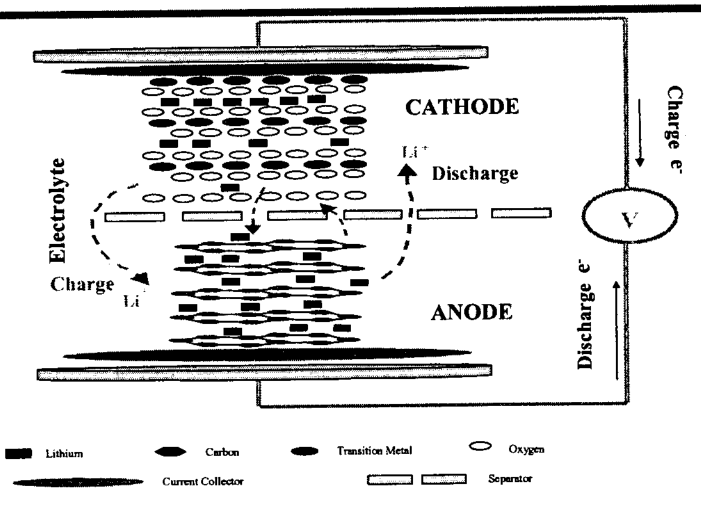
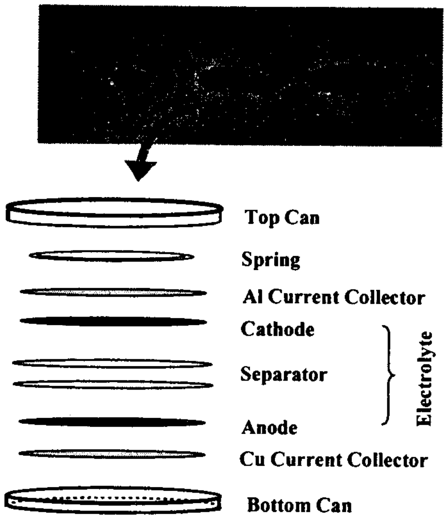
Electrochemical Reaction of the "Rocking Chair" Li-Ion Battery



A Coin-type Cell Assembly



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Properties of Electrolyte Solvents

Solvent		ε	η (cP)	M. P. (°C)	B. P. (°C)
Alkyl Carbonate	EC (Ethylene Carbonate)	89.6 (40 oC)	1.86 (40 oC)	36.4	238
	DMC (Dimethyl Carbonate)	3.12	0.59	4.6	90
	DEC (Diethyl Carbonate)	2.82	0.75	-43	127
	PC (Propylene Carbonate)	64.4	2.5	-49	241
Ether	THF (Tetrahydrofuran)	7.6	0.48	-108.5	65
	DME (1,2-dimethoxyethane)	5.5	0.45	-58	82.5
~~Ester~~	~~γ-BL~~ (γ-Butyrolactone)	~~39~~	~~1.75~~	~~-43~~	~~204~~

ε: Dielectric constant at 25 °C, η: viscosity at 25 °C,
M. P. melting point, B. P. boiling point at 760 Torr

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Safety Concerns of Li-ion Batteries

- **Thermal runaway**
  - **–High power discharge**
  - **–Overcharge**
  - **–Abusive and cell-shorting conditions**
- **Heat and pressure build-up within the cell**
- **Cell fire caused by the flammable electrolyte**
- **Large-scale batteries for electric and hybrid electric vehicles (EV/HEV)**

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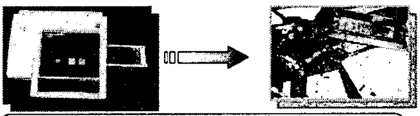
Is Still Li Battery Safe?



U.S., LIFEPAK® 500 automated external defibrillator (AED) Using Li Battery

Korea, Used Li Battery

Thailand, Nokia 3310

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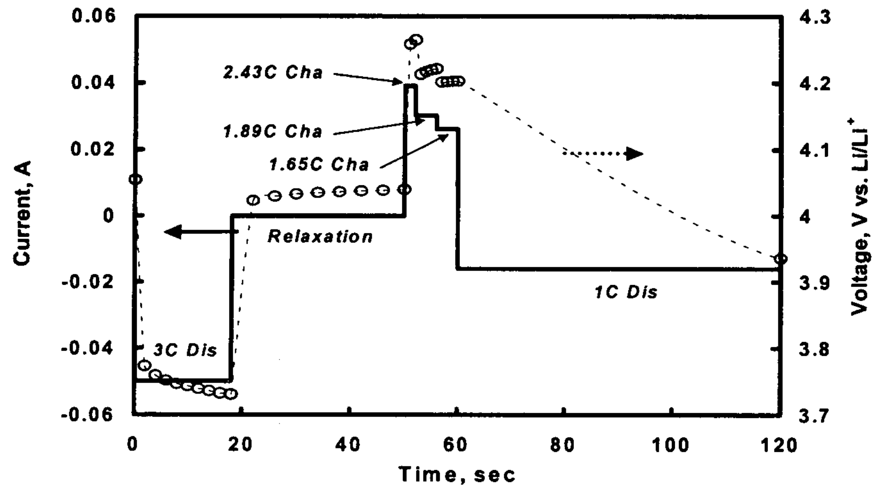
Voltage Response Corresponding to Hybrid Pulse Power Characterization (HPPC) Profile for EV/HEV Applications



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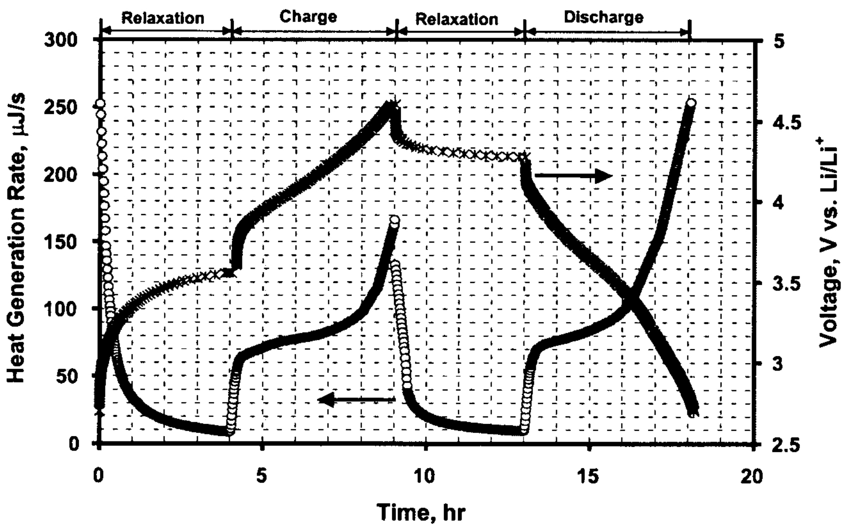
In-Situ Calorimetric Profiles of Li-ion Battery



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Strategy for the Safety Design

- Develop new electrolyte systems
  - Improved salts
  - Change the organic liquid solvents

- Modify the existing electrolytes by incorporation of a flame-retardant (FR) additive

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Salts

- $LiPF_6$ (Lithium Hexafluorophosphate)
- $Li(CF_3SO_2)_2N$ (Lithium bis-trifluoromethylsulfonyl imide)
- $LiCF_3SO_3$ (Lithium trifluoromethanesulfate)

- **To study the influence of different salts on the thermal properties of electrolytes**

- **To determine corrosion rate of respective electrolyte systems**

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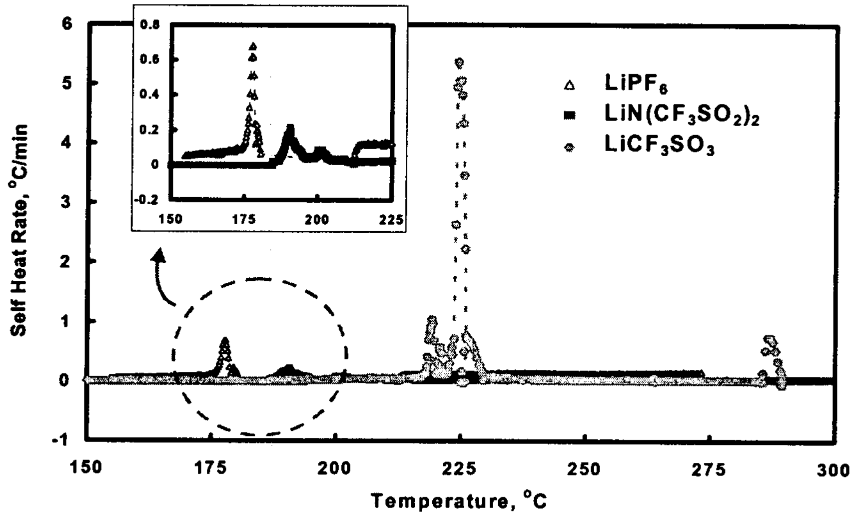
Self-Heat Rates of Respective Electrolytes using ARC



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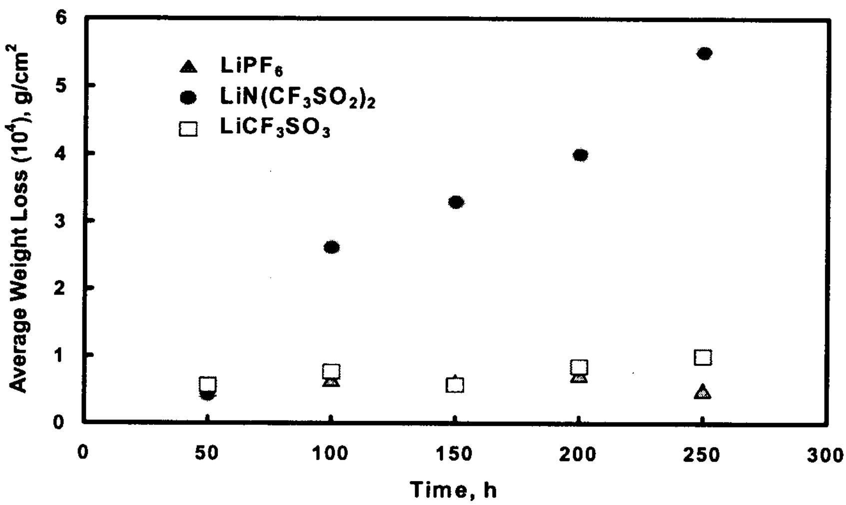
Corrosion of Aluminum Current Collector Caused by Electrolytes



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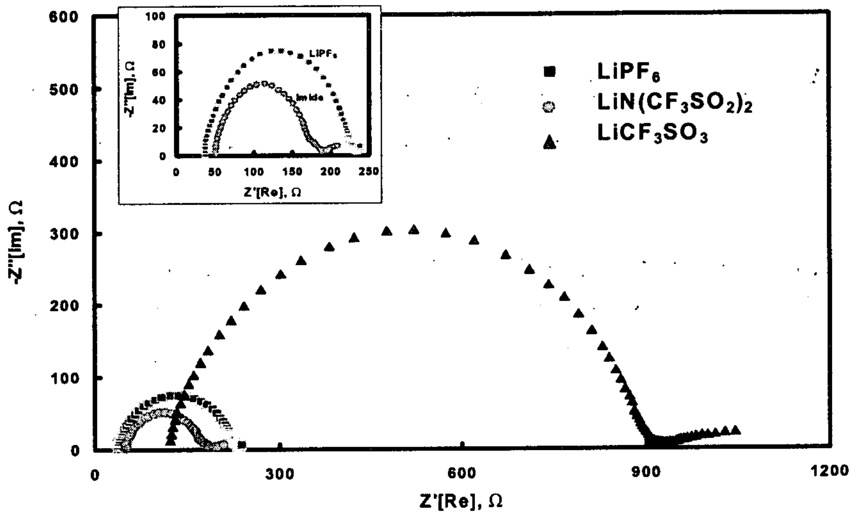
Complex Plane A.C. Impedance Spectra of the Li-Li Symmetrical Cells with Different Electrolytes



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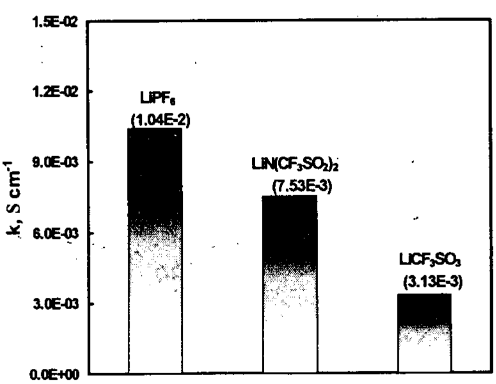
Ionic Conductivity κ of the Electrolytes at Ambient Temp.

$$L = \kappa\left(\frac{A}{l}\right) \quad [S, \Omega^{-1}]$$

$$L = R^{-1}$$

$$\kappa = \frac{l}{z' A} \quad [\Omega^{-1}cm^{-1}]$$



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Nonflammable Electrolyte

- To synthesize Hexamethoxycyclotriphosphazene $[NP(OCH_3)_2]_3$ as a novel flame-retardant additive

- To investigate the electrochemical and thermal properties of the electrolyte systems modified by incorporation of the flame-retardant additive in the electrolyte

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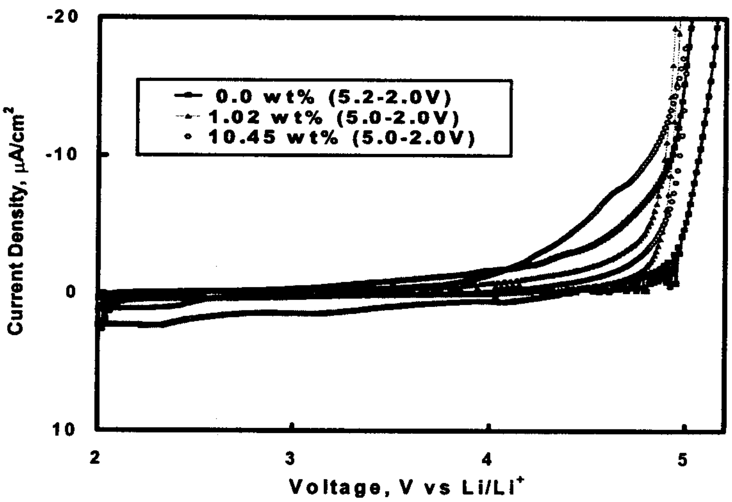
Cyclic Voltammograms of a Glassy Carbon Electrode containing 0.0, 1.02, and 10.45 wt% of HMTP



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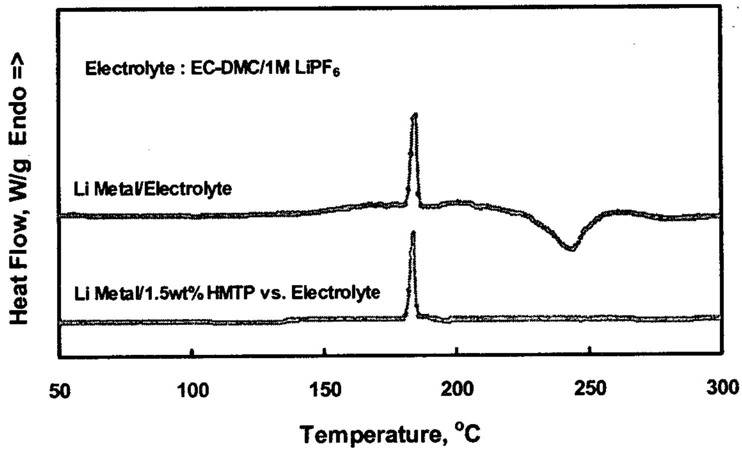
A Comparison of Thermal Behavior using DSC for Effect on Addition of the HMTP



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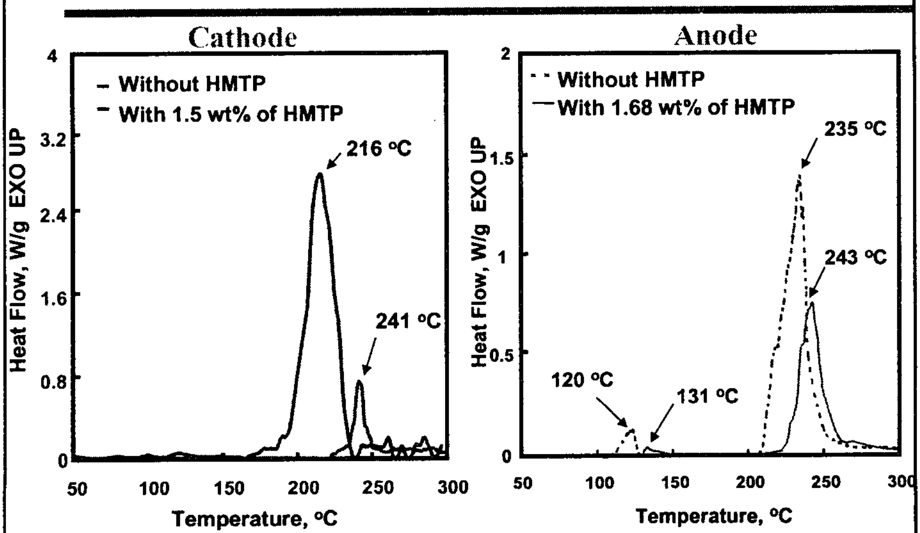
Thermal Behavior of fully Delithiated $LiNi_{0.8}Co_{0.2}O_2$ Cathode and Lithiated Graphite Anode With and Without HMTP using DSC



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Conclusions

- Hexamethoxycyclotriphosphazene $[NP(OCH_3)_2]_3$ as a flame-retardant additive was synthesized
- Cyclic voltammetry results show that the electrolyte containing the flame-retardant additive is electrochemically stable up to 5.0 V
- Modification of existing electrolyte system using flame-retardant additive helps for shifting onset temperature of SEI layer decomposition
- The reduced heat flow and the self-heat rate corresponding to the addition of HMTP as the flame-retardant additive help in improving the thermal stability, and hence the nonflammability of the electrolyte

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